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# PATENT ABSTRACTS OF JAPAN

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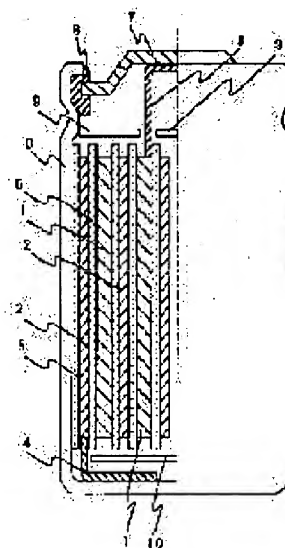
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## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To enhance the cycle reliability and storage stability of a lithium secondary battery by using a nonaqueous electrolyte of a solvent containing the specified amount of a specific non-conjugated unsaturated cyclic hydrocarbon compound in the secondary battery having a carbon material negative electrode and a lithium-containing oxide positive electrode.

**SOLUTION:** A belt-shaped negative electrode 2 made of a carbon material such as flake high crystallized graphite capable of absorbing/releasing lithium and a belt-shaped positive electrode 1 made of a lithium-containing oxide such as  $\text{LiCoO}_2$  are stacked and wound through a porous separator 5. The spirally wound electrode body obtained is housed in a battery container 6 together with a nonaqueous electrolyte, and lead terminals 3, 4 are fixed to obtain a nonaqueous electrolyte lithium secondary battery. As a solvent occupying 80-90% of the nonaqueous electrolyte, ethylene carbonate or the like is used, and 10-20vol.% non-conjugated unsaturated cyclic hydrocarbon compound having a plurality of double bonds and 6-12 carbon atoms is added to the ethylene carbonate or the like. As the solute of the nonaqueous electrolyte, a lithium salt such as lithium hexafluorophosphate is used.



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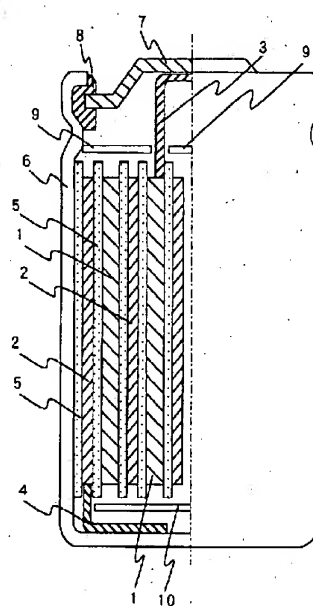
(54) 【発明の名称】 非水電解液二次電池

(57) 【要約】

【構成】非水電解液二次電池の電解液の溶媒に10～20体積%の二重結合を複数個有する炭素数6以上、12以下の側鎖を持たない非共役環状炭化水素、例えば、1,5-シクロオクタジエン等を添加する。溶媒は環状カーボネート類と、鎖状カーボネート、または、環状エーテル、または、ラクトン類との1:1混合物とする。

【効果】非共役環状炭化水素を電解液に含有することにより、炭素負極への挿脱入時、充電貯蔵時の安定性が高くなり、サイクル及び貯蔵寿命が向上する。

図 1



## 【特許請求の範囲】

【請求項1】リチウムを吸蔵、放出可能な炭素材から成る負極と、非水電解液と、リチウム含有酸化物から成る正極を備える非水電解液二次電池において、前記非水電解液の溶媒に二重結合を複数個有し、炭素数が6以上、12以下の非共役不飽和環状炭化水素化合物を10～20体積％含むことを特徴とする非水電解液二次電池。

【請求項2】請求項1において、前記非水電解液の80～90体積％を占める前記溶媒が、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネートの10 中から選ばれた溶媒と、ジエチルカーボネート、ジメチルカーボネート、メチルエチルカーボネート、γ-ブチロラクトン、1,3-ジオキサソラン、テトラヒドロフラン中から選ばれた溶媒との一対一の混合物である非水電解液二次電池。

【請求項3】前記負極炭素の材料が、六方晶構造を99％以上有し、炭素の層間長であるX線回折における層間長 $d_{002}$ が0.336nm以下で、結晶厚み $L_c$ が25～30nmの値を有し、その比表面積が $20\text{m}^2/\text{g}$ 以上と大きな薄片状の高結晶性黒鉛からなる請求項1または2に記載の非水電解液二次電池。

【請求項4】前記正極の活物質がリチウムとコバルトの複合酸化物、リチウムとニッケルの複合酸化物、リチウムとマンガンの複合酸化物、リチウムと鉄の複合酸化物、或いは、リチウムと遷移金属との複合酸化物である請求項1、2または3に記載の非水電解液二次電池。

【請求項5】前記非水電解液がその溶質として、六フッ化リン酸リチウム、ホウフッ化リチウム、過塩素酸リチウム、トリフロロメタンスルホン酸リチウム、六フッ化砒酸リチウムのうち少なくとも一つを含む請求項1、2、3または4に記載の非水電解液二次電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は非水電解液二次電池に関する。

## 【0002】

【従来の技術】近年、移動体通信やラップトップコンピュータの普及はめざましく、これら電子製品の電源用途として繰り返し充放電が可能な二次電池の需要も飛躍的に伸びている。これらは携帯用の製品であり、電源にも軽量、小型、高容量等の性能が求められる。更に、これら製品の多機能化により、高電圧化が求められている。これらの要求を満たす電源として非水電解液二次電池、特に、リチウム二次電池は高電圧、高エネルギー密度を有する電池として盛んに研究・開発されている。リチウム二次電池の高エネルギー密度を実現する正極活物質は、 $\text{LiMn}_2\text{O}_4$ 、 $\text{LiCoO}_2$ 、 $\text{LiNiO}_2$ 、 $\text{LiFeO}_2$ 等のリチウムの複合酸化物が挙げられる。

【0003】一方、負極にはリチウム金属、リチウム合金やリチウムを吸蔵、放出可能な炭素材料が用いられて

いる。リチウム金属やリチウム合金を負極に用いた場合には、リチウムの電析による電極表面のデンドライドの生成や電極の膨張・収縮による劣化などが発生する問題がある。これに対し、炭素材料ではリチウムイオンが炭素材の層間にインターカレート、デカレートすることにより充放電を行うので、金属や合金における問題は解決する。しかし、充電電位を4V以上に設定して充放電サイクルを繰り返したり、充電状態で長期間貯蔵すると特性が劣化する。これは、特開平4-332479号公報、特開平4-249870号公報、特開平4-337258号公報、特開平4-337247号公報などに示されている様に、高電圧による電解液、特に、非水溶媒の分解劣化に起因すると思われる。つまり、層間脱挿入型の電極であっても表面での電気化学的な反応は避けられない状況にある。従って、4V級の高容量リチウム二次電池の性能を向上し、かつ、サイクル特性や保存信頼性を向上するには、非水電解液の特性改良が不可欠となっている。

【0004】電解液改良の方法として、特定の化合物を添加する方法が多く公開されている。例えば、特開平4-332479号公報では過充電を防止するためにメチルベンゼン類を10容量％添加することが記されている。また、特開平4-249870号公報には、トルエンを添加することにより充電貯蔵安定性を向上させる方法が記されている。これらの電解液の改良に使用される添加剤の多くはそれら自体の反応性を利用して溶媒の分解反応を防止しようとするものである。

## 【0005】

【発明が解決しようとする課題】しかし、この様な方法では添加剤自体が反応した場合に、添加剤が減少してその効果が低下したり、余分な反応生成物が電解液内に残存してしまう可能性がある。そこで、発明者らはそれ自体も安定であり、且つ、主溶媒の反応を抑制する様な添加剤が必要であると考えた。

【0006】本発明の目的は、自己分解のない安定な添加剤を加えた電解液組成を提供し、リチウム二次電池のサイクル信頼性及び貯蔵安定性を向上することにある。

## 【0007】

【課題を解決するための手段】まず、溶媒の分解がリチウム金属やリチウム合金を負極とした場合でも起こること、或いは、炭素負極の場合では分子径の大きな環状分子の方が鎖状分子よりも分解し易いこと、更には、充放電サイクルの初期に電極表面に反応生成物の被膜が形成されるとサイクル特性が向上するため、炭素負極で溶媒の分解反応は電極表面で進行すると考えた。一方、溶媒分子がリチウムイオンに配位すると、分子内の電子密度分布が変化する。これまで非水電解液二次電池に使用されている溶媒であるカーボネート類、ラクトン類、エーテル類、及び、エステル類は分子内の酸素原子により、その不対電子を介してリチウムイオンに配位すると考えられる。これらの溶媒はリチウムイオンに配位した際

に、酸素の隣の炭素原子の電子密度が極端に低下する。このため、充電時に配位酸素の隣の炭素が還元反応を受けやすくなっている。つまり、分子径の大きな溶媒はリチウムイオンに溶媒和した状態でコインターカレートできないため、負極近くに留まる確率が増え、配位酸素の隣の炭素が還元される確率が高くなり、分解し易いと考えた。

【0008】以上の考察に基づき、酸素や窒素等の原子上の不対電子によらずリチウムイオンへの溶媒和が可能で、且つ、溶媒和した状態で炭素層間にコインターカレート可能な物質が安定な、溶媒の分解防止のための添加剤になり得ると考えた。そこで、酸素や窒素等の軽元素ヘテロ原子を含まない化合物に注目し、これらの条件を満たす添加剤を検索した。その結果、二重結合を複数個有する、炭素数6以上かつ12以下の不飽和環状炭化水素が $\pi$ 電子供与により、リチウムイオンを溶媒和できることを見出した。具体的には、1, 3-シクロヘキサジエン、1, 4-シクロヘキサジエン、1, 3-シクロヘプタジエン、シクロヘプタトリエン、1, 5-シクロオクタジエン、1, 5, 9-シクロデカトリエン等が使用できる。これらの化合物は、いわゆる、共役二重結合を形成しないのでリチウムイオンに配位する際に、分子形状を変形することが可能でイオンを包み込む様に配位することができる。また、配位力も酸素原子による配位力に近く、カーボネート等の溶媒とも協奏的にリチウムイオンに配位できる。更に、これらの分子がリチウムに配位する際の最小径は炭素材料の層間隔である0.336 nm よりも小さく、電極近くで環状溶媒等の大きな分子を脱離して炭素層間にコインターカレートすることができる。また、配位分子の形状がリチウムイオンを包んだ扁平形状になるので炭素層の内表面と比較的広い面積で吸着でき、配位分子を伴った形で、安定なキャパシタを形成することが可能である。つまり、安定な充電状態を実現できる。

【0009】上記の化合物は液相温度範囲も広く非水溶媒としての能力も十分であるが、炭化水素化合物は誘電率が低く電解液の導電率が確保しにくいので、これらの化合物は添加剤としての利用が有効である。その添加量は電解液中のリチウム塩濃度とはほぼ等しい濃度とすることが効果的であり、具体的には、1モル/リットルの濃度の電解液中に10~20体積%の添加が望ましい。

【0010】

【作用】本発明の非共役不飽和環状炭化水素の電解液添加剤は、リチウムイオンに配位した際の分子内の電子密度変化が小さく、安定な溶媒和構造を実現できる。更に、溶媒和構造の最小径が小さいので炭素負極の層間にコインターカレートして溶媒を伴った形の吸着層を形成でき、安定な充電状態を達成させる。

【0011】

【実施例】以下、本発明を円筒型非水電解液二次電池に

適用した実施例について詳細に説明する。

【0012】(実施例1) 図1に本実施例で作製する円筒型非水電解液二次電池を示す。まず、帯状正極1を以下の通り作製した。市販の炭酸リチウムと炭酸コバルトを、組成比Li/Coが1となるように混合し、空気中で900℃で7時間焼成して、リチウム・コバルト酸化物LiCoO<sub>2</sub>を得た。このリチウム複合酸化物を正極活物質として90重量%、導電剤として黒鉛を6重量%、結着剤としてポリフッ化ビニリデンを4重量%を混合し、更に、N-メチル-2-ピロリドンを加えて混練してペースト状にした。このペーストを帯状アルミニウム箔の両面に塗布し、プレス乾燥して帯状正極1を作製した。

【0013】次に、帯状炭素負極2を以下の通り作製した。炭素材料として薄片高結晶黒鉛(日立化成製)を90重量%、結着剤としてポリフッ化ビニリデンを10重量%を混合し、更に、N-メチル-2-ピロリドンを加えて混練してペースト状にした。このペーストを帯状の銅箔の両面に塗布し、プレス乾燥して帯状負極2を作製した。

【0014】尚、正極1及び負極2には集電するため、それぞれアルミニウム製の正極リード端子3と、ニッケル製の負極リード端子4とを接続してある。この様にして作製した正極1及び負極2を、これらの間にポリプロピレン製のマイクロポラスフィルムからなるセパレータ5を介在させながら互いに積層し、多数回巻回して、渦巻型の電極体を作った。

【0015】この電極体を、ニッケル・メッキを施した鉄製の電池容器6に収納し、負極リード端子4を、電池容器6の内底部にスポット溶接により接続し、正極リード端子3を電池封口板7に同様にして接続した。

【0016】電解液として、エチレンカーボネート：ジエチルカーボネート：1, 5-シクロオクタジエンの割合が、体積比で45：45：10になるように調製した溶媒に六フッ化リチウムを1モル/リットル溶解した溶液を作製した。この電解液を電極を収納した電池容器6に注液し、該電池容器6と電池封口板7とをポリプロピレン製パッキン8を介して嵌合してかしめ、密封することで、円筒型非水電解液二次電池を作製した。尚、この電池の外寸法は、外径20mm、高さ60mmであり、容量は900mAhであった。

【0017】(実施例2) エチレンカーボネート：ジエチルカーボネート：1, 5, 9-シクロデカトリエンの割合が、体積比で45：45：10になるように調製した溶媒に六フッ化リチウムを1モル/リットル溶解した溶液を電解液とした。

【0018】(実施例3) エチレンカーボネート：ジエチルカーボネート：1, 3-シクロペンタジエンの割合が、体積比で45：45：10になるように調製した溶媒に六フッ化リチウムを1モル/リットル溶解した溶液

を電解液とした。

【0019】(実施例4) エチレンカーボネート：ジエチルカーボネート：シクロペンタトリエンの割合が、体積比で45：45：10になるように調製した溶媒に六フッ化リチウムを1モル／リットル溶解した溶液を電解液とした。

【0020】(実施例5) エチレンカーボネート：ジエチルカーボネート：1，3-シクロヘキサジエンの割合が、体積比で45：45：10になるように調製した溶媒に六フッ化リチウムを1モル／リットル溶解した溶液を電解液とした。

【0021】(実施例6) エチレンカーボネート：ジエチルカーボネート：1，4-シクロヘキサジエンの割合が、体積比で45：45：10になるように調製した溶媒に六フッ化リチウムを1モル／リットル溶解した溶液\*

表 1

試料	サイクル試験300回後の容量維持率 (%)	貯蔵試験後の閉回路電圧 (V)	貯蔵試験後の容量維持率 (%)
実施例1	84	4.01	86
実施例2	82	4.01	84
実施例3	81	3.98	83
実施例4	82	3.93	81
実施例5	77	3.98	73
実施例6	76	3.98	72
比較例1	55	3.85	60

【0025】表1から明らかな様に、非共役不飽和環状炭化水素を含む電解液を使用した実施例1～6の二次電池は、これを含まない比較例1の二次電池に比べて、サイクル特性、充電貯蔵安定性ともに向上している。但し、実施例5及び6の特性が若干悪いのはこれらの添加剤の沸点が90℃以下と低いことに起因するものと考え

る。

【0026】

【発明の効果】本発明は非共役不飽和環状炭化水素を含※

\*を電解液とした。

【0022】(比較例1) エチレンカーボネート：ジエチルカーボネートの割合が、体積比で50：50になるように調製した溶媒に六フッ化リチウムを1モル／リットル溶解した溶液を電解液とした。

【0023】これらの二次電池に関して、定電流充電300mAで4.2Vまで充電した後、以下の評価をした。充放電サイクル試験として、0.5Cの定電流充放電を300サイクル行い、試験後の容量保持率を評価した。また、充電貯蔵試験として、充電状態で室温で500時間貯蔵した後、0.2C定電流放電を行い、開回路電圧及び容量維持率を調べた。これらの結果を表1に示す。

【0024】

【表1】

※む溶媒を非水電解液二次電池の電解液にすることにより、電池のサイクル及び充電貯蔵寿命が改善される。

【図面の簡単な説明】

【図1】本発明の非水電解液二次電池の一実施例を示す縦断面図。

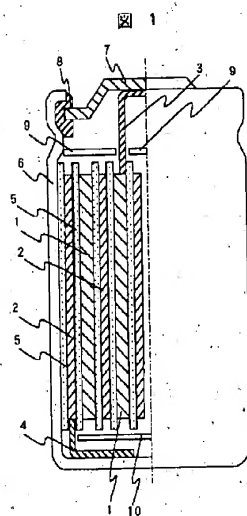
【符号の説明】

1…常状正極、2…常状負極、3…正極リード端子、4…負極リード端子、5…セパレータ、6…電池容器、7…電池封口板、8…パッキン、9、10…絶縁板。

(5)

特開平9-35746

【図1】



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**CLAIMS**

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[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by 10-20 volume % Having two or more double bonds in the solvent of the aforementioned nonaqueous electrolyte, and a carbon number containing 6 or more and 12 or less disconjugation unsaturation cyclic-hydrocarbon compound in a nonaqueous electrolyte rechargeable battery equipped with the negative electrode which consists of the carbon material which emits [ occlusion and ] a lithium, nonaqueous electrolyte, and the positive electrode which consists of a lithium content oxide.

[Claim 2] The nonaqueous electrolyte rechargeable battery which is the mixture of an one to one with the solvent with which the aforementioned solvent which occupies 80 - 90 volume % of the aforementioned nonaqueous electrolyte was chosen in the claim 1 from the solvent chosen from ethylene carbonate, propylene carbonate, and butylene carbonate, diethyl carbonate and dimethyl carbonate, methylethyl carbonate, gamma-butyrolactone, 1, 3-dioxolane, and the tetrahydrofuran.

[Claim 3] The material of the aforementioned negative-electrode carbon has hexagonal structure 99% or more, the merit d002 between layers in the X diffraction which is the carbonaceous merit between layers has the value whose crystal thickness Lc is 25-30nm by 0.336nm or less, and the specific surface area is 20m<sup>2</sup>/g. Nonaqueous electrolyte rechargeable battery according to claim 1 or 2 which consists of a high crystallinity graphite of the above and a big thin film integrated circuit.

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 1, 2, or 3 whose active material of the aforementioned positive electrode is the multiple oxide of a lithium, the multiple oxide of cobalt and a lithium, the multiple oxide of nickel and a lithium, the multiple oxide of manganese and a lithium, and iron, or the multiple oxide of a lithium and transition metals.

[Claim 5] The nonaqueous electrolyte rechargeable battery according to claim 1, 2, 3, or 4 with which the aforementioned nonaqueous electrolyte contains at least one of a 6 fluoride [ phosphoric-acid ] lithium, hoe lithium fluoride, a lithium perchlorate, lithium triphloromethanesulfonate, and 6 fluoride arsenic-acid lithiums as the solute.

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[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] In recent years, the spread of mobile communications or laptop computers is remarkable, and the need of the rechargeable battery in which charge and discharge are possible is also repeatedly extended by leaps and bounds as a power supply use of these electronic product. These are portable products and a power supply is also asked for performances, such as lightweight, small, and high capacity. Furthermore, high-voltage-ization is called for by multi-functionalization of these products. Research and development especially in a lithium secondary battery is briskly done as a power supply which fills these demands as a nonaqueous electrolyte rechargeable battery and a cell which has a high voltage and high-energy density. the positive active material which realizes high-energy density of a lithium secondary battery --  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiFeO}_2$  etc. -- the multiple oxide of a lithium is mentioned

[0003] On the other hand, the carbon material which emits [ occlusion and ] a lithium metal, a lithium alloy, and a lithium is used for the negative electrode. When a lithium metal and a lithium alloy are used for a negative electrode, there is a problem which generation of the DIN drama id on the front face of an electrode by the electrocrystallization of a lithium, degradation by expansion and contraction of an electrode, etc. generate. On the other hand, in a carbon material, since a lithium ion performs charge and discharge intercalation and by carrying out a deca rate between the layers of carbon material, the problem in a metal or an alloy is solved. However, if charge potential is set up more than 4V, a charge-and-discharge cycle is repeated or a long term storage is carried out in the state of charge, a property will deteriorate. This is considered to originate in decomposition degradation of the electrolytic solution by the high voltage, especially a non-aqueous solvent as shown in JP,4-332479,A, JP,4-249870,A, JP,4-337258,A, JP,4-337247,A, etc. That is, even if it is a layer indirect desulfurization insertion type electrode, the electrochemical reaction in a front face is in the situation which is not avoided. Therefore, in order to improve the performance of a 4V class high capacity lithium secondary battery and to improve a cycle property and preservation reliability, property improvement of nonaqueous electrolyte is indispensable.

[0004] Many methods of adding a specific compound as the method of electrolytic-solution improvement are exhibited. For example, by JP,4-332479,A, in order to prevent a surcharge, doing 10 capacity % addition of methylbenzenes is describing. Moreover, the method of raising charge storage stability is describing by adding toluene at JP,4-249870,A. Many of additives used for improvement of these electrolytic solutions tend to prevent the decomposition reaction of a solvent using the reactivity of these very thing.

[0005]

[Problem(s) to be Solved by the Invention] However, by such method, when the additive itself reacts, additives decrease in number, the effect may fall or an excessive resultant may remain in the electrolytic solution. Then, artificers' itself is also stable and they thought that an additive which suppresses the reaction of the main solvent was required.

[0006] The purpose of this invention offers the electrolytic-solution composition which added the stable additive without an autolysis, and is to improve the cycle reliability and storage stability of a lithium secondary battery.

[0007]

[Means for Solving the Problem] First, happening, even when disassembly of a solvent uses a lithium metal and a lithium alloy as a negative electrode or that it is easy to decompose the big cyclic molecule of the diameter of a molecule rather than a chain molecule by the case of a carbon negative electrode, and since a cycle property would improve further if the coat of a resultant is formed in an electrode front face in early stages of a charge-and-discharge cycle, I thought that the decomposition reaction of a solvent advanced on an electrode front face by the carbon negative electrode. On the other hand, if a solvent molecule configures in a lithium ion, the electron density distribution in a molecule will change. It is thought that the carbonate which is the solvent used for the nonaqueous electrolyte rechargeable battery until now, lactone, ether, and ester are configured in a lithium ion through the unpaired electron with the oxygen atom in a molecule. When these solvents are configured in a lithium ion, the electron density of the carbon atom of the next door of oxygen falls extremely. For this reason, the carbon of the next door of coordination oxygen is easy to receive a reduction reaction at the time of charge. That is, since the big solvent of the diameter of a molecule was not able to carry out a coin TAKA rate where a solvation is carried out to a lithium ion, the probability of stopping near the negative electrode increased, the probability that the carbon of the next door of coordination oxygen would be returned became high, and I thought that it was easy to decompose.

[0008] Based on the above consideration, it was not based on the unpaired electron on atoms, such as oxygen and nitrogen, but the solvation to a lithium ion was possible, and where a solvation is carried out, I thought that it might become an additive for the decomposition prevention of a solvent with the stable matter in which a coin TACA rate is possible between carbon layers. Then, the additive which fulfills these conditions was searched paying attention to the compound which does not contain light element hetero atoms, such as oxygen and nitrogen. Consequently, six or more carbon numbers and 12 or less unsaturation cyclic hydrocarbon which have two or more double bonds found out that the solvation of the lithium ion could be carried out by pi-electron supply. Specifically, 1, 3-cyclohexadiene, 1, 4-cyclohexadiene, 1, 3-cycloheptadiene, cycloheptatriene, 1, 5-cyclo-octadiene, 1 and 5, 9-cyclododecatriene, etc. can be used. Since the so-called conjugated double bond is not formed, in case it configures in a lithium ion, these compounds can transform a molecular shape, and they can be configured so that ion may be wrapped in. Moreover, solvents, such as near and carbonate, can also configure the coordination force in concertante performance in the coordination force by the oxygen atom at a lithium ion. Furthermore, the diameter of the minimum at the time of these molecules configuring in a lithium is 0.336nm which is the interlayer spacing of a carbon material. It is small, and it is desorbed from big molecules, such as an annular solvent, near the electrode, and a coin TACA rate can be carried out between carbon layers. Moreover, since the configuration of a coordination molecule turns into the flat configuration where the lithium ion was wrapped, it can adsorb in latus area comparatively with the internal surface of a carbon layer, and it is a form accompanied by the coordination molecule, and it is possible to form a stable capacitor. That is, a stable charge state is realizable.

[0009] Although the liquid phase temperature requirement of the capacity as a non-aqueous solvent is [ the above-mentioned compound ] also widely enough, since a dielectric constant is low and the conductivity of the electrolytic solution cannot secure a hydrocarbon compound easily, these compounds have the effective use as an additive. As for the addition, it is effective to consider as concentration almost equal to the lithium salt concentration in the electrolytic solution, and, specifically, its addition of 10 - 20 volume % is desirable in the electrolytic solution with a concentration of one mol [l. ].

[0010]

[Function] The electrolytic-solution additive of the disconjugation unsaturation cyclic hydrocarbon of this invention has the small electron density change in the molecule at the time of configuring in a lithium ion, and can realize stable solvation structure. Furthermore, since the diameter of the minimum of solvation structure is small, between the layers of a carbon negative electrode, a coin TACA rate is carried out, the adsorption layer of the form accompanied by the solvent can be formed, and a stable charge state is made to attain.

[0011]

[Example] Hereafter, the example which applied this invention to the cylindrical nonaqueous electrolyte rechargeable battery is explained in detail.

[0012] (Example 1) The cylindrical nonaqueous electrolyte rechargeable battery produced by this example to drawing 1 is shown. First, the band-like positive electrode 1 was produced as follows. A commercial lithium carbonate and commercial cobalt carbonate are mixed so that composition ratio Li/Co may be set to 1, and it calcinates at 900 degrees C in air for 7 hours, and is the lithium cobalt oxide  $\text{LiCoO}_2$ . It obtained. By making this lithium multiple oxide into a positive active material, the polyvinylidene fluoride was mixed for the graphite as an electric conduction agent 90% of the weight, and 4 % of the weight was mixed as 6 % of the weight and a binder, and further, the N-methyl-2-pyrrolidone was added and kneaded and it was made the shape of a paste. This paste was applied to both sides of a band-like aluminum foil, press dryness was carried out, and the band-like positive electrode 1 was produced.

[0013] Next, the band-like carbon negative electrode 2 was produced as follows. The polyvinylidene fluoride was mixed for the flake quantity crystal graphite (Hitachi Chemical make) as a carbon material, and 10 % of the weight was mixed as 90 % of the weight and a binder, and further, the N-methyl-2-pyrrolidone was added and kneaded and it was made the shape of a paste. This paste was applied to both sides of band-like copper foil, press dryness was carried out, and the band-like negative electrode 2 was produced.

[0014] In addition, in order to collect a current to a positive electrode 1 and a negative electrode 2, the positive-electrode lead terminal 3 made from aluminum and the negative-electrode lead terminal 4 made from nickel are connected to them, respectively. Thus, the laminating was carried out mutually, making the separator 5 which consists of a micro porous film made from polypropylene among these the positive electrode 1 and negative electrode 2 which were produced intervene, it \*\*\*\*(ed) many times, and the swirl type electrode object was made.

[0015] This electrode object was contained in the iron cell container 6 which performed nickel plating, the negative-electrode lead terminal 4 was connected to the low section by spot welding among the cell containers 6, and the positive-electrode lead terminal 3 was similarly connected to the cell obturation board 7.

[0016] As the electrolytic solution, the solution which dissolved one mol /of 6 lithium fluoride in the solvent of ethylene carbonate:diethyl carbonate:1 and 5-cyclo-octadiene comparatively prepared so that it might be set to 45:45:10 by the volume ratio 1. was produced. This electrolytic solution was poured in the cell container 6 which contained the electrode, this cell container 6 and the cell obturation board 7 were fitted in through the packing 8 made from polypropylene, and the cylindrical nonaqueous electrolyte rechargeable battery was produced by the caulking and sealing. In addition, the dimension of this cell was 60mm in the outer diameter of 20mm, and height, and capacity was 900mAh(s).

[0017] (Example 2) ethylene carbonate: -- diethyl carbonate: -- the solution which dissolved one mol /of 6 lithium fluoride in the solvent of 1, 5, and 9-cyclododecatriene comparatively prepared so that it might be set to 45:45:10 by the volume ratio 1. was made into the electrolytic solution

[0018] (Example 3) ethylene carbonate: -- diethyl carbonate: -- the solution which dissolved one mol /of 6 lithium fluoride in the solvent of 1 and 3-cyclopentadiene comparatively prepared so that it might be set to 45:45:10 by the volume ratio 1. was made into the electrolytic solution

[0019] (Example 4) ethylene carbonate: -- diethyl carbonate: -- the solution which dissolved one mol /of 6 lithium fluoride in the solvent of cyclo PENTA trien comparatively prepared so that it might be set to 45:45:10 by the volume ratio 1. was made into the electrolytic solution

[0020] (Example 5) ethylene carbonate: -- diethyl carbonate: -- the solution which dissolved one mol /of 6 lithium fluoride in the solvent of 1 and 3-cyclohexadiene comparatively prepared so that it might be set to 45:45:10 by the volume ratio 1. was made into the electrolytic solution

[0021] (Example 6) ethylene carbonate: -- diethyl carbonate: -- the solution which dissolved one mol /of 6 lithium fluoride in the solvent of 1 and 4-cyclohexadiene comparatively prepared so that it might be set to 45:45:10 by the volume ratio 1. was made into the electrolytic solution

[0022] Ethylene carbonate: (Example 1 of comparison) The solution which dissolved one mol /of 6 lithium fluoride in the solvent of diethyl carbonate comparatively prepared so that it might be set to 50:50 by the volume ratio 1. was made into the electrolytic solution.

[0023] these rechargeable batteries -- being related -- 300mA of constant-current charge -- 4.2V up to -- the following evaluations were carried out after charging As a charge-and-discharge cycle examination, it is 0.5C. The capacity retention after a 300 cycle deed and an examination was evaluated for constant-current charge and discharge. Moreover, 0.2C after storing at a room temperature in the state of charge as a charge storage examination for 500 hours Constant-current discharge was performed and open-circuit voltage and the capacity maintenance factor were investigated. These results are shown in Table 1.

[0024]

[Table 1]

表 1

試料	サイクル試験300回 後の容量維持率 (%)	貯蔵試験後の開 回路電圧 (V)	貯蔵試験後の容 量維持率 (%)
実施例 1	84	4.01	86
実施例 2	82	4.01	84
実施例 3	81	3.98	83
実施例 4	82	3.93	81
実施例 5	77	3.98	73
実施例 6	76	3.98	72
比較例 1	55	3.85	60

[0025] Compared with the rechargeable battery of the example 1 of comparison which does not contain this, a cycle property and charge storage stability of the rechargeable battery of the examples 1-6 which used the electrolytic solution containing a disconjugation unsaturation cyclic hydrocarbon are improving so that clearly from Table 1. However, the thing with the property of examples 5 and 6 bad a little thinks that the boiling point of these additives originates in 90 degrees C or less and a low thing.

[0026]

[Effect of the Invention] When this invention makes the solvent containing a disconjugation unsaturation cyclic hydrocarbon the electrolytic solution of a nonaqueous electrolyte rechargeable battery, the cycle and charge storage life of a cell are improved.

[Translation done.]